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CONDUCTIVE MINERALIC COATING
FOR ELECTROCHEMICAL CORROSION
PROTECTION OF STEEL REINFORCEMENT
IN CONCRETE

TRANSLATOR'S DECLARATION

Commissioner for Patents
P.O. Box 1450
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Sir:

I, Kari O. Hanssen, declare:

that I am thoroughly familiar with both the Norwegian and English languages;

that the attached document represents a true English translation of Norwegian Priority Application 19990509 filed February 4, 1999; and

That I further declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

January 7, 2004
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Kari O. Hanssen
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Conductive mineral coating for electrochemical corrosion protection of steel reinforcement in concrete

The present invention relates to a conductive mineral coating used for electrochemical corrosion protection of steel reinforcement in concrete. More specifically, the invention relates to a method for electrochemical protection of reinforcement in concrete in harsh environments, as well as to a use of a conductive coating for the protection of concrete in such environments.

It has been known for many decades that inorganic binders such as cement, in particular Portland cement, which have alkaline properties, protect metals containing iron against corrosion. Due to this corrosion-inhibiting effect it has been possible to make reinforced concrete where the steel is embedded in the concrete, and it has not been necessary to apply any protection, for example, in the form of protective paint, to the steel.

The corrosion-inhibiting effect of cement is due to the formation of calcium hydroxide during the hydration, which gives a pH value of 12 and more in the cement paste.

When cement is carbonated, which means that carbon dioxide from the air reacts with calcium hydroxide, the pH value may fall dramatically. At pH values of less than 9 the steel reinforcement will start to corrode.

Corrosion is accelerated by the formation of cracks in the building material as well as by the effect of chlorides from contaminated aggregates, de-icing salts, air pollution and seawater.

A method for preventing corrosion of steel in concrete is to polarise the steel cathodically (cathodic protection, electrochemical chloride removal, electrochemical realkalisation), where the steel is the cathode, or the negative pole, and an external anode is the positive pole. As such external anodes use has been made of Ti-meshes, wires or rods coated with mixed metal oxides, electrically conductive asphalt, flame-sprayed zinc or titanium and conductive paints. A conductive paint has two major advantages. First, it does not add extra weight to the structure, which may be a problem for slender structures from a statistic point of view. Secondly, the conductive paint provides excellent current distribution.

The existing paints are mainly composite materials with a polymer (acrylates, latex, polystyrene and the like) as a film-forming binder (vehicle) and graphite as filler –

so-called skeleton conductors. Because of a combination of damp conditions, as mentioned above, and the electrochemical reactions which take place at the paint-concrete interface, the paints lose their adhesion to the concrete base, which leads to failure of the electrochemical treatment.

It has also been known for several decades that silicate-based mineral paints react with the substrate (plaster, concrete, natural stone etc.) by petrification. This means that the water-soluble silicates penetrate the mineral substrate to which they have been applied and form a chemical microcrystalline bond therewith, in contrast to film-forming paints which form a surface skin.

In US Patent No. 4,035,265, Saunders describes a conductive paint which can be applied to walls and the like for heating purposes. The paint composition contains carbon particles and flakes of graphite, and also a hardenable binder which may be an inorganic silicate binder, an organic ammonium silicate binder or, for example, an organic solvent soluble resin binder. Due to the intended use as a source of heat, this paint contains large amounts of graphite or carbon particles.

The problems described above are aggravated in environments where humidity is high, and in particular in contact with, or in close proximity to, seawater. Studies in such areas often show substantial corrosion damage. Examples of such areas include the thousands of quay structures which are subject to reinforcement corrosion. Many of these quay structures cannot be closed, even for a short time, because of daily use.

The only way to solve this problem in existing quay structures has been cathodic protection, preferably using Ti meshes embedded in shotcrete, installed under the quay. This is a time-consuming and very costly procedure. Often, the layers applied are subject to delamination. The use of conductive paint systems in such wet and humid environments will not work because of delamination or blistering of the anode film.

The object of the present invention is to propose a new solution to these problem, more specifically to provide an easily applicable, mechanically and electrochemically stable anode solution which also functions well in humid environments and in close proximity to, or in contact with, seawater.

Accordingly, the present invention provides a method for electrochemical protection of reinforcement in concrete in harsh environments, for example, in contact with, or in

natural stone surfaces. When the cathodic protection installation is energised, the voltage field that arises will cause migration of ions which leads to further curing and strengthens the anode. This is per se a known phenomenon. Due to the strength of the cured coating the graphite particles will be completely immobilised and function as a well-established skeleton, thereby providing a highly conductive anode for electrochemical treatments. Since the solution or dispersion of the mineral compounds used in the coating is highly alkaline, the delamination effects due to the acidification of the coating-concrete interface during the electrochemical process at the anode are strongly reduced. A conventional anode with a latex or acrylic binder will, in contrast, lose adhesion over time because of this process. This is a very important difference since acid will be produced at the anode concrete on cathodic protection. With the alkaline coating a reservoir against acid formation will be obtained, which is a highly desirable effect since, as is common knowledge, acid dissolves concrete.

In view of the aforementioned effect, tests have been conducted to examine the difference in development of adhesion between the coating of the present invention and an anode based on a latex or acrylic binder.

Another positive effect caused by this type of anode for cathodic protection (CP) is that the electrical field will draw alkali ions from the paint by electrophoretic movement. This leads to an increased degree of polymerisation of the silica gel, which will thus become increasingly water-resistant. After some time, a completely insoluble matrix of silicate hydrogel (SiO x H O) will be formed as binder. The silicate coating according to the invention therefore is useful as an anode in the cathodic protection of very damp structures such as the underside of quay structures, harbour installations or bridge piers in seawater where conventional skeleton conductors thus far have failed.

According to one possible embodiment of the present invention, a catalyst may be added to the coating. Examples of substances that may be used as catalyst include precious metals, heterocyclic compounds with interstitial metal atoms etc. It has been found the doping the graphite with precious metals prevents oxidation of the graphite. The coating containing graphite doped with precious metals has a reduced overpotential for the anodic reaction compared with undoped paint. In particular, doped graphite in combination with the silicate binder as described has proven to be a highly suitable CP anode in humid or wet environments.

close proximity to, seawater, characterised in that an agent comprising graphite dispersed in water glass or another inorganic silicate, a dispersing agent and optionally conventional additives, is applied to the concrete by spraying or brushing, and impregnation is optionally effected either simultaneously with, or after, the application of the aforementioned agent.

Unlike the known mineral paints, it has been found that the coating according to the invention does not form a film on the surface to which it is applied. It does, however, react with the outer layer of the concrete surface, diffuses into the pores and hardens into a conductive impregnation. An acid-resistant interface in the adhesion zone between the applied product and the concrete is obtained.

One factor of importance for the lifetime of an anode is that the transition resistance between concrete and anode is as low as possible. The present invention results in a reduced transition resistance compared with anodes consisting of synthetic paints (binders), (cf. Example 3).

The coating according to the invention may easily be sprayed on the concrete surface using conventional paint guns or it can be brushed onto the concrete surface using conventional equipment.

Another new and important feature of the coating according to the invention is that the non-filmed, treated surface obtained can be impregnated with non-film forming impregnating agents to repel water and remain dry. Optionally, the impregnating agent may be incorporated into the coating so that the whole anode can be applied to the concrete surface concerned in one operation

As mentioned above, the coating according to the invention contains graphite or carbon particles in a mineral matrix. As in conventional skeleton conductors, the graphite particles contact each other in this material to provide electric conductivity.

The mineral matrix consists basically of silicates, preferably in the form of water glass, with or without additives in the form of aluminates, calcium hydroxide or other gelling agents. The mineral components are used basically as solutions or dispersions, but can also be used as solid compounds. The mineral composition will penetrate the outer concrete layer and form a gel-like material in the pores and on the concrete surface and will therefore, when the water evaporates, adhere strongly to concrete, masonry and

As mentioned above, the concrete surface treated with the coating according to the invention, because of the porous character of the surface, can be impregnated after the application or optionally simultaneously therewith, with a low viscosity solution of, for example, silanes or siloxanes in order to render it hydrophobic. Since silanes or siloxanes will be an integral part of the silica gel, long-term hydrophobic behaviour may be expected, which thus will result in an increased lifetime for the anode.

Because of the impregnation-like character of the coating according to the invention, delamination problems will not occur on the use of the present invention.

EXAMPLES

The following, non-limiting examples give the composition of coatings according to the invention.

Example 1

A coating of the following composition was prepared:

175 parts potassium silicate solution K35
5 parts carbon black dispersion (25%)
2 parts detergent
50 parts graphite
5 parts calcium hydroxide

The water glass reactive component, calcium hydroxide, must be added to the coating a few hours before the coating is to be applied.

Example 2

A coating of the following composition was prepared:

175 parts potassium silicate solution K35
10 parts carbon black dispersion (25%)
2 parts detergent
1 part "Aerosil"
4 parts potassium hydroxide
60 parts graphite
11 parts sodium aluminate (5% solution)

The water glass reactive component, sodium aluminate, must be added to the composition a few hours before the coating is to be applied.

Below is a table which summarises the present method seen in comparison with the methods used previously.

Subject	Present invention	Comment	Normal anode	Comment
Binder	Water glass		Latex/acrylic	
Waterproof?	Yes		No/partly	
Is binder oxidised?	No	Silicate cannot oxidise	Yes	Oxidation of graphite/binder "Slack" after a while
Acid resistance under the anode?	Yes	Silicate = increased resistance	No	Pure concrete not acid-resistant
Does it withstand water when in use, give lasting adhesion?	Yes	Test now. Adb.increases, device hardens further when current applied	No	Delaminates, short lifetime
Does it form a film, ie, prevent diffusion?	No		Yes	Film formation is a problem in wet areas
Can it be impregnated, water-repellent?	Yes	Both before and after	No	Plastic prevents impregnation
Conductivity?	High	No plastic	Lower	Insulating plastic
Shrinkage	No	Little water	Yes	Water-based
Transition resistance?	Low	Graphite-gel interface	Higher	Because of plastic/less graphite against concrete

Patent claims

1.

A method for electrochemical protection of concrete in harsh environments, for example, in contact with, or in close proximity to seawater, characterised in that an agent comprising graphite dispersed in a curable mineral binder, in the form of water glass or another water-soluble inorganic silicate, a dispersing agent and optionally conventional additives, is applied to the concrete by spraying or brushing, and impregnation is optionally carried out, either simultaneously with, or after the application of the aforementioned agent.

2.

A method according to claim 1, characterised in that the agent applied, as additives, comprises additives which act as a curing agent.

3.

A method according to claim 2, characterised in that the additive contains one or more of the components calcium hydroxide, sodium aluminate and/or sodium bicarbonate.

4.

A method according to the preceding claims, characterised in that the impregnation is effected with a silane or siloxane solution of low viscosity.

5.

Use of a coating comprising graphite dispersed in a curable mineral binder, in the form of water glass or another water-soluble inorganic silicate, a dispersing agent and optionally conventional additives, for cathodic protection of reinforcement in concrete.

6.

Use according to claim 5, wherein the coating, as additives, contains additives which act as a curing agent.

7.

Use according to claim 6, wherein the additive contains one or more of the components calcium hydroxide, sodium aluminate and/or sodium bicarbonate.

8.

Use according to claim 5, wherein the impregnation is effected with a silane or siloxane solution of low viscosity.

9.

Use according to claims 5-8 for cathodic protection of reinforcement in concrete in connection with quay structures, bridges, bridge piers and the like.

Abstract

A method is described for the electrochemical protection of reinforcement in concrete in harsh environments, for example, in contact with, or in close proximity to, seawater, characterised in that an agent comprising graphite dispersed in a curable mineral binder, in the form of water glass or another water-soluble organic silicate, a dispersing agent and optionally conventional additives, is applied to the concrete by spraying or brushing, and impregnation is optionally effected, either simultaneously with, or after, the application of the aforementioned agent.
The use of the coating for electrochemical protection of reinforcement in concrete in, for instance, quay structures, bridges bridge piers and the like, is also described.